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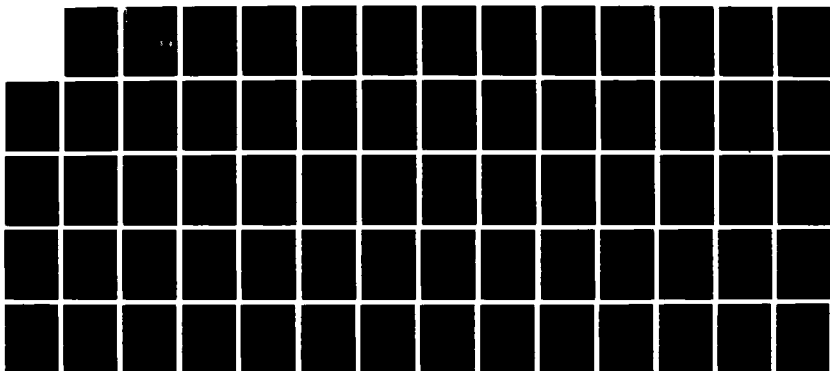
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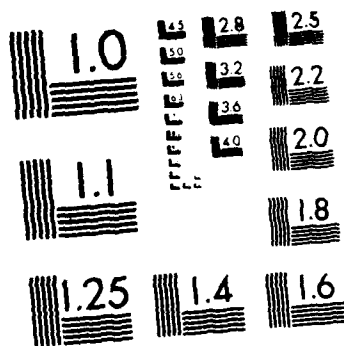
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"A General, Qualitative Study of Point and  
Extended Defects and Their Interactions  
in Non-metallic Systems"

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## Abstract

In this report we describe progress in developing and implementing a general theoretical approach to describing the properties of defects and impurities of a general nature in non-metallic solid systems. Also we review progress in complementary non-destructive experimental tests. These tests employ and extend newly developed techniques in EPR and NMR imaging in solids. First of a kind EPR imaging experiments have been performed, and a new NMR imaging laboratory has been constructed.



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## Introduction

The aim of this research is to characterize point and extend defects and to elucidate their role in initiating chemical processes. The research is being carried out in two separate but interacting branches. The theoretical thrust is to develop a methodology for obtaining absolute energies of defects (impurity ions, charged states and low lying excited states) in solids. From these studies a model for the initiation of energetic materials is being formulated. These two issues are reviewed in the first two sections of this report. The first section outlines the possible role of charged defects in initiating energetic reactions. The second section reviews progress made in creating a self consistent algorithm for calculating total energies of defects in solids.

The experimental thrust of this program is to develop, implement, and exploit non-invasive techniques for imaging in solids. The two experimental techniques that are being developed are: Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR). An NMR imaging laboratory has been constructed under the direction of one of the Principal Investigators (B. H. Suits). An outline of the strategies used to construct the NMR laboratory is included in the third section of this report. The last two sections of this report deal with the recently developed EPR imaging techniques. First of a kind EPR imaging was performed under the direction of one of the Co-investigators (S. A. Marshall). This research is outlined in section four of this report. The last section of this report deals with EPR spectroscopy of magnetic defects in solids.

## Theory Sub-project Progress

### BACKGROUND: $\text{NH}_4\text{ClO}_4$

Ammonium perchlorate is a white crystalline solid which undergoes a reversible crystallographic transition from a low-temperature orthorhombic structure to a cubic structure at  $240^\circ\text{C}$  ( $513^\circ\text{K}$ ). [1-4] This polymorphic change is attributable to the onset of free rotation of the perchlorate anions. [5,6] The low-temperature bipyramidal orthorhombic form has cell dimensions  $a_o = 9.202 \text{ \AA}$ ,  $b_o = 5.816 \text{ \AA}$ ,  $c_o = 7.449 \text{ \AA}$ . [7] The cubic high-temperature form [8-9] contains four molecules per unit cell which has a cube edge of  $7.63 \text{ \AA}$ . The calculated density [10] of the cubic form is  $1.76 \text{ g/cm}^3$  [5], as compared with  $1.95 \text{ g/cm}^3$  [11] for the measured density of the low-temperature form. The phase transition from orthorhombic to cubic is endothermic and is accompanied by a significant amount of decomposition and heat generation. [12] The computed heat of transition from the orthorhombic to the cubic crystal structure is  $2.3 \pm 0.2 \text{ kcal/mole}$ . [10] There is some uncertainty as to the effect of the phase transition on the kinetics of ammonium perchlorate decomposition. Bircumshaw and Newman [13] first observed that the maximum decomposition rate rose sharply to a maximum at  $238^\circ$ , then fell to a minimum at  $250^\circ$ , and finally increased again. Rate constants for the cubic form were substantially lower than those for the orthorhombic form Shidlovskii, et al., [14] and Manelis and Rubtsov [15] have also reported that the kinetic description of the decomposition curves depends on the crystal form. In the decomposition of the cubic modification above  $240^\circ$  decomposition centers are initiated by growth of a single nucleus (rather than

by aggregation), are spherical in form, and are randomly distributed throughout the body of the crystal. The activation energy for nucleus growth is  $17 \pm 1$  kcal/mole. [12] There apparently has been little work done on the role of dislocations in the decomposition of ammonium perchlorate. The effect of heating ammonium perchlorate to the decomposition temperature is to increase the dislocation density in the vicinity of a nucleus. Least-mean-square values for the activation energies are  $33.91 \pm 1.64$  kcal/mole for orthorhombic and  $26.97 \pm 2.36$  kcal/mole for the cubic modification. [16] The question of the precise effect of the phase transition on the decomposition is still an open one.

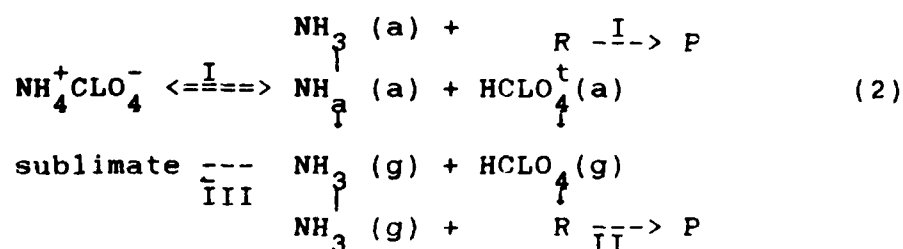
Bircumshaw and Newman [17,18] considered three possible mechanisms for the decomposition of ammonium perchlorate. They are

1. Electron transfer from a  $\text{ClO}_4^-$  anion to an (interstitial)  $\text{NH}_4^+$  cation.
2. Proton transfer from  $\text{NH}_4^+$  to  $\text{ClO}_4^-$ .
3. Thermal breakdown of  $\text{ClO}_4^-$  anions by rupture of a Cl-O bond.

They ascribed the high-temperature reaction to (3), sublimation to (2), and the low-temperature reaction to (1).

Jacobs and Russell-Jones [19] however indicate that a single unified mechanism is operative in both the low- and high-temperature decomposition and for sublimation. That unified mechanism they believe to be proton transfer. They represent the various modes of decomposition of ammonium perchlorate by the following scheme.





I denotes the Low-temperature mechanism, II the high-temperature mechanism, and III the sublimation process. (a) denotes the adsorbed state and (g) the gas phase. R denotes radical intermediates and P the final products. The rate of decomposition is faster than the sublimation. [12] The low-temperature reaction must therefore involve adsorbed  $\text{NH}_3$  and  $\text{HClO}_4$ . Early observations of nucleation [20] indicate that certain crystal sites are preferentially involved. This indicates the role of impurities or of imperfections in initiating this reaction. Since the low-temperature reaction is suppressed in specially purified ammonium perchlorate, [21] impurities rather than dislocations [22] are indicated as nucleus-forming sites. If the temperature of the residue is raised,  $\text{NH}_3$  desorbs from the crystal surface and the high-temperature reaction sets in. The distinction between this reaction and sublimation is whether or not the  $\text{HClO}_4$  decomposes in the gas phase. The situation gets markedly more complicated when catalysts and/or inhibitors and polymeric fuels are involved. In general catalysts lower the minimum ignition temperature. A unified treatment of the mathematical theories of ignition is available in a survey article by Price, et al. [35]

The unified mechanism [19] proposed by Jacobs and Russell-Jones (equation 2) has the  $\text{NH}_4^+ \text{ClO}_4^-$  going to neutral  $\text{NH}_3$  and  $\text{HClO}_4$ . Isolating this change of state and structure was explored

by Cardy, et al. [32] They make a theoretic prediction of the kinetic parameters of the radical formation and dissociation reactions. The ground state of the ammonium radical appears to be of the Rydberg type. They found its ionization potential to be 4.29 eV., the  $\text{NH}_4$  formation reaction from  $\text{NH}_3 + \text{H}$  to be slightly endothermic. They predict a lifetime for  $\text{NH}_4$  of 0.1  $\mu\text{s}$ .

Ng and Jacobs in their paper on thermal depolarization in ammonium chloride crystals [36] propose that protons transfer from the  $\text{NH}_4^+$  to form the molecular defect,  $\text{NH}_3 + \text{HCL}$ . The HCL is then mobile in the anion sublattice because of the mobility of the trapped protons. At the surface HCL molecules escape, leaving behind anion vacancies, which diffuse into the crystal and eventually trap the mobile proton holes. Anion vacancies are known to be mobile from diffusion experiments. HCL diffuses down grain boundaries and dislocations as HCL molecules, and then into the crystal as protons in the anion sublattice. Once the protons annihilate the proton holes the anion vacancies liberated diffuse to dislocations and annihilate the cation vacancies produced when HCL enters the lattice. Perhaps this or a similar mechanism is operative in ammonium perchlorate also.

Harris and Fiasson [37] in their paper on the measurement of surface and boundary charge on NaCl state, "The difference between the Gibbs free energies required for anion and cation vacancy formation in an ionic crystal produces an excess of vacancies of one sign at source and sinks of vacancies, and hence causes dislocations, surfaces and grain boundaries to become charged." With a relatively simple apparatus they determined the potential on freshly cleaved surfaces of nominally pure, single crystal NaCl

to be negative at room temperature. They found the potential near grain boundaries in bicrystals to be positive. They attribute the difference to grain boundary precipitation and predict a boundary isoelectric point at higher temperatures. The presence of charges, both positive and negative, can be predicted for the ionic ammonium perchlorate crystal.

The existence of the  $\text{NH}_4$  radical, at least in the gaseous state, appears no longer in doubt. The Rydberg Spectrum has been observed and interpreted by G. Herzberg. [33] He states, "On the basis of the observed vibration spectrum its generally agreed that the  $\text{NH}_4^+$  ion has tetrahedral structure (point group  $T_d$ ). If an electron is added in a Rydberg orbital one may expect the same  $T_d$  structure for the resulting neutral  $\text{NH}_4$  radical in its Rydberg states."

The ab initio calculations of Kaspar, Smith and McMaster [34] on the potential barrier for the dissociation of the ammonium radical



proved very helpful to this work. Their published values of 56.55903 hy. for uncorrelated energy and -56.77444 hy. for correlated system energy of  $\text{NH}_4^+$  compares favorably with our free radical energies of -56.403662 hy. and -56.506768 hy. respectively. Their calculations employed Slater type orbitals and CI energy corrections. Their CI correlation accounts for 0.221541 Hy. or 56.86 eV. compared to 0.1031455 Hy. or 2.81 eV. for our MBPT correction. The difference between their calculated

value at the UHF level and ours was 0.15541 Hy. or 4.23 eV. The difference at the correlated level was 0.26767 Hy. or 7.28 eV.

## THEORY - UHF

Ab initio unrestricted Hartree-Fock linear combination of atomic orbital (LCAO) theory is the method used in this study to calculate energy values. We are primarily interested in the electronic characteristics of molecular solids. The problem can be divided into two parts, that involving motion of nuclei and that involving the electrons. [24]

$$H \Psi = E \Psi \quad (4)$$

is the Schroedinger Wave Equation. The hamiltonian,  $H$ , operates on the wave function,  $\Psi$ , giving the total energy,  $E$ .  $E$  is the sum of the potential energy and kinetic energy of the system. This hamiltonian can be written as

$$H = H_{el} + H_{nuc} = H_{el-nuc} \quad (5)$$

$el$  represents the electron contributions,  $nuc$  the contributions from interactions of the different nuclei with each other, and  $el-nuc$  the electron-nuclei portion. Effects from the external environment are neglected.

$$H_{el} = \sum_{i=1}^n -\frac{1}{2} \nabla_i^2 + \sum_{i \neq j}^n -\frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (6)$$

$$H_{nuc} = -\sum_{i=1}^N -\frac{1}{2M_i} \nabla_i^2 + \sum_{j \neq k}^N \frac{Z_j Z_k}{R_{jk}} \quad (7)$$

$$H_{el-nuc} = -\sum_{k=1}^N \sum_{i=1}^n -\frac{Z_k}{|R_k - r_i|} \quad (8)$$

$n$  is the number of electrons.  $r$  describes the electron

coordinates.  $N$  is the number of nuclei,  $R$  their coordinates,  $M$  their mass, and  $Z$  their charge. The nuclei are assumed infinitely massive and the Born-Oppenheimer (adiabatic) approximation employed. The calculations then involve only the average positions of the nuclei [24] and  $H_{\text{el-nuc}}$  is redefined as  $H_{\text{el-nuc}}^0$ . The equation for the motion of the electrons then becomes

$$(H_{\text{el}} + H_{\text{el-nuc}}^0) \psi(r) = E_{\text{el}} \psi(r) \quad (9)$$

This is the electronic Schroedinger wave equation. It is assumed the total wave function,  $\Psi$ , can be approximated by a product of nuclear and electron wavefunctions. [25] The wave function is redefined as  $\psi$  and, it will be shown, is a function of both position and spin.

Hartree-Fock theory approximates the wave function,  $\psi$ , as a finite linear combination of Slater determinants. [26]

$$\psi = \sum_i C_i \Delta_i \quad (10)$$

$\Delta_i$  is a Slater determinant and is a convenient way to invoke the Pauli Exclusion Principle. We use only a single Slater determinant which consists of products of spin orbitals,  $\phi_i$ .

$$\Delta = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \dots & \phi_n(1) \\ \vdots & & \vdots \\ \phi_1(n) & \dots & \phi_n(n) \end{vmatrix} \quad (11)$$

$1/\sqrt{n!}$  is for normalization.  $n$  is the number of electrons. The determinant allows for all possible permutations of electrons, each electron being indistinguishable from any other is equally likely to occupy any available spin orbital. Note, exchanging two electrons interchanges two columns resulting in a sign change for

the determinant. The wave function is said to be antisymmetric with respect to the interchange of two particles. Also, if two electrons have the same space and spin coordinates, two of the columns are identical, the determinant equals zero; ie. the wavefunction vanishes.

The unrestricted version of hartree-Fock theory (UHF) has no symmetry restrictions imposed on  $\phi$  other than they be eigenstates of  $s_z$ . A single determinant of doubly occupied orbitals represents a totally symmetric singlet ground state of an atom or molecule. Apparently most molecular ground states are of this type. [23] Singlet ground state energy changes are an objective of this study.

The expectation value of the energy for a given Hamiltonian and wave function is an upper limit to the true energy.

$$E = \frac{\langle \Delta | H | \Delta \rangle}{\langle \Delta | \Delta \rangle} \geq E_{\text{true}} \quad (12)$$

A variational method is applied to minimize the energy hence giving the best approximation to the wavefunction. The  $\phi$ 's are varied until the minimum energy is found.

$$\frac{\partial E}{\partial \phi_i} = 0 \quad (13)$$

The  $\phi_i$  are constrained to be orthonormal. The orbitals are not required to be doubly occupied or to have well defined symmetry. When the  $\phi_i$  are determined variationally, they are determined by the Hartree-Fock equation:

$$F(\rho) \phi_i = \epsilon_i \phi_i \quad (14)$$

$F$  is the Fock operator and  $\rho$  is the first order density matrix.

The total energy then becomes

$$E = \sum_i \epsilon_i \quad (15)$$

The nuclei are assumed infinitely massive and the Born-Oppenheimer approximation employed.

The Hamiltonian in the Born-Oppenheimer approximation is

$$H = -\frac{1}{2} \sum_k \nabla_k^2 + \sum_k \sum_i \frac{Z_k}{|R_k - r_i|} + \frac{1}{2} \sum_{k,j} \frac{1}{|R_k - R_j|} + \sum_{k,j} \frac{Z_k Z_j}{|R_k - R_j|} \quad (16)$$

using atomic units where  $e = \eta = 1$  and 1 hartree = 27.2 eV.  $Z_{k,j}$  is the atomic number of the nucleus at site  $R_{k,j}$ .  $r_{i,k,j}$  define the electron coordinates. There are  $n$  electrons and  $N$  nuclei in the system. The last term is a constant because nuclear motion is being neglected. When the nuclei are assumed fixed, kinetic energy is zero and the potential energy constant. The solution to an eigenvalue problem is invariant respecting the addition of a constant, once this potential energy term is calculated, it can be stored and added back into the total energy solution when needed.

Equation (8) can also be written

$$H = \sum_{i=1}^n F_i + -\frac{1}{2} \sum_{i \neq j} g_{ij} \quad (17)$$

where  $F_i$  are the one-electron operators and  $g_{ij}$  represents the two-electron operators, coulomb and exchange. The energy is then:

$$E = \sum_{i=1}^n \langle \phi_i(1) | F | \phi_i(1) \rangle + -\frac{1}{2} [ \langle \phi_i(1) \phi_j(2) | g_{12} | \phi_i(1) \phi_j(2) \rangle - \langle \phi_i(1) \phi_j(2) | g_{12} | \phi_j(1) \phi_i(2) \rangle ] \quad (18)$$

Use of the energy variational principle and varying  $E$  with respect



to the  $\phi_k$ , applying Lagrangian multipliers for the orthonormality constraint on solutions, one can write the Hartree-Fock equation:

$$F_1 \phi_k(1) + \sum_j \left[ \int \phi_j^*(2) \phi_j(2) d\tau_2 \phi_k(1) - \int \phi_j^*(2) g_{12} \phi_k(2) d\tau_2 \phi_j(1) \right] = E_k \phi_k(1) \quad (19)$$

or

$$H^{scf} \phi_k = E_k^{scf} \phi_k \quad (20)$$

where  $H^{scf}$  is the self consistent field Hamiltonian operator. The equations are then solved iteratively, the Hartree-Fock Hamiltonian operator being a function of the solutions,  $\phi_k$ .

## THEORY - MBPT

Calculation of the energy corrections is accomplished by taking the unrestricted Hartree-Fock (UHF) solution as the starting point and then apply the variant of Raleigh-Schroedinger perturbation theory, Many Body Perturbation Theory (MBPT). The single Slater determinant is enhanced by perturbation theory to include correlation and by a projection technique to produce eigenstates of  $S^Z$ .

The exact Hamiltonian can be represented by the simplified Hamiltonian,  $H^0$ , whose eigenvalues and eigenfunctions are known and a perturbation,  $V$ .

$$H = H^0 + V \text{ so, } V = H - H^0 \quad (21)$$

The known eigenvalues and eigenfunctions are the zeroth order result of the UHF self consistent field calculations in this study. They may be represented as

$$H^0 \phi_j = \omega_j \phi_j \quad (22)$$

ie.

$$E_j^0 = \omega_j = \langle \phi_j | H^0 | \phi_j \rangle \quad (23)$$

The first order correction is the expectation value,  $E_j^1$ , of the perturbation of the unperturbed state. Second order corrections require that the wavefunction be correct to first order.

$$E_j^1 = \langle \phi_j | V | \phi_j \rangle = V_{00} \quad (24)$$

additionally,

$$E_j^0 + E_j^1 = E_{\text{UHF}} \quad (25)$$

The second order correction to energy which we seek is

$$E_j^2 = \langle \phi_j | V | \phi_j^1 \rangle \quad (26)$$

where  $\phi_j^1$  is the first order wavefunction. Defining the particular state we seek as  $\psi_0$  which yields energy,  $E_0$ , which are both unknown, then

$$H\psi_0 = E_0\psi_0 = (H^0 + V)\psi_0 \quad (27)$$

Applying the known eigenvalues and eigenfunctions of  $H^0$  we may write

$$(H^0 - \omega_0)\psi_0 = (E_0 - V - \omega_0)\psi_0 \quad (28)$$

The inverse operator,  $(H^0 - \omega_0)^{-1}$ , could then be used to determine  $\psi_0$ . However the function being operated upon must have no projection on to  $\phi_0$ , otherwise singularities can occur. The projector,  $P$ , will project out of  $\psi_0$  a part of  $\phi_0$  so that singularities will no occur.

$$P = |\phi_0\rangle\langle\phi_0| \quad (29)$$

Multiplying by the projection operator,  $(1 - P)$

$$(1 - P) (H^0 - \omega_0) \psi_0 = (1 - P) (E_0 - V - \omega_0) \psi_0 \quad (30)$$

Defining and applying intermediate normalization

$$\langle \psi_0 | \phi_0 \rangle = 1 \quad (31)$$

then, after some rearrangement

$$\psi_0 = [1 - (H^0 - \omega_0)^{-1} (1 - P) (E_0 - V - \omega_0)]^{-1} \phi_0 \quad (32)$$

This in turn results in a power series for  $\psi_0$ . Developing an expression for the energy,  $E_0$

$$\langle \phi_0 | H | \psi_0 \rangle = \langle \phi_0 | E_0 | \psi_0 \rangle \quad (33)$$

or

$$\langle \phi_0 | H^0 | \psi_0 \rangle + \langle \phi_0 | V | \psi_0 \rangle = \langle \phi_0 | E_0 | \psi_0 \rangle \quad (34)$$

Solving yields

$$E_0 = \omega_0 + \langle \phi_0 | V | \psi_0 \rangle \quad (35)$$

Replace  $\psi_0$  with the power series expansion, construct  $V$  in terms of the  $\phi_1$ , then

$$V_{00} = \langle \phi_0 | V | \phi_0 \rangle \quad (36)$$

However,  $E_0$  is part of the solution and must be replaced by its first order expression. Let  $E_0 \approx w + V_{00}$ , then to second order

$$E_0 = \omega_0 + V_{00} + \sum_{j \neq 0} \frac{V_{0j} V_{j0}}{\omega_0 - \omega_j} = \omega_0 + V_{00} + E_0^2 \quad (37)$$

This is the form desired for second order corrections. It has been shown [27] that this procedure, MBPT, gives about 90% of the correlation energy available in a given basis set.

## EXPERIMENT

The ammonium portion of ammonium perchlorate as a free radical in the presence of a negative point charge has been studied in a previous work. [1] The intent of this study is to extend investigation of the negative point charge defect phenomenon to the crystal structure and expand it to include vacancy type defects.

Crystalline ammonium perchlorate has two temperature dependent forms. Low temperature orthorhombic and high temperature cubic. High temperature cubic was selected as the object of this study.

The unrestricted Hartree-Fock calculation utilizes the linear combination of atomic orbitals (LCAO) approximation to construct the spin orbitals. That is

$$\phi_i = \sum_j c_{ij} \chi_j \quad (38)$$

$c_{ij}$  is an appropriately chosen unitary matrix.  $\chi_j$  are primitive Gaussian type orbitals (GTO's).

$$\chi_j = a_j \left[ x^l y^m z^n e^{-b_j r} \right] \quad (39)$$

$a_j$  and  $b_j$  are input parameters for the POLYATOM computer code utilized for calculation of integrals over atomic orbitals.  $x^l$ ,  $y^m$ , and  $z^n$  represent the type of atomic orbital, s, p, d, f, etc.  $\chi_j$  are primitive Gaussians. Contracted basis functions used in this study are linear combinations of primitive gaussians. [29]

The  $\text{NH}_4^+$  molecule was constructed from Huzinaga atomic basis sets. [30] The exception is hydrogen which is the Dunning and Hay [31] contraction H(1s) of the Huzinaga H(4s) uncontracted to H(3s/1s) to give additional freedom to the system.

All variations in the charge array were made at the location

of the first point charge on the negative z-axis, (0,0-7.0338 a.u.), which was a negative charge. The configuration of the radical was not altered from its tetrahedral form found in the orthorhombic configuration. The intent is to study the tetrahedral  $\text{NH}_4^+$  radical [33] at a lattice site and then to vary the immediate environment. The hydrogen designated H1 located at (0,0,-1.915 a.u.) was moved incrementally down the z-axis. UHF +  $E^2$  correlation energy, and Mullikan populations were monitored.

### Analysis of Results:

The chemical decomposition of a system such as  $\text{NH}_4\text{ClO}_4$  is a complex issue. One might be interested for instance in the removal of H (or  $\text{H}^+$ ,  $\text{H}^-$ ) from the  $\text{NH}_4^+$  unit or of O (or  $\text{O}^-$ ) from  $\text{ClO}_4^-$  and even in the formation of OH,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , HCl etc. In the initial case presented here, we consider the possible removal of  $1+$  from an  $\text{NH}_4$  unit, making it available for further reaction. The results presented here are for the UHF + MBPT results only. In the case of a perfect crystal, a barrier of 3.5445 eV exists to the removal of a hydrogen. This is seen in the figure labeled  $\text{NH}_4^+$  5x5x5 array - no defects. Here the z-axis extends from the N of an  $\text{NH}_4$  to the Cl of a nearest  $\text{ClO}_4$ . If the nearest neighbor  $\text{ClO}_4^-$  is removed from the lattice creating an anion vacancy (a common type lattice defect) the barrier to H removal is raised to 5.87 eV as is seen in the figure labeled Vacancy Defect. In this case the defect has a net positive charge. If however the  $\text{ClO}_4^-$  is replaced by a double negative ion, yielding a net negative region the barrier to H removal drops to 1.3245 eV (a substantial drop, and at distance close to the  $\text{NH}_4^+$  is exothermic). In this case the H is removed as a proton this is seen in the figure - chag. defect.

This latter case is quite important as it shows the presence of a net negative region promoting the lowering of a barrier to chemical change. However this is still not quite realistic. Usually in a crystal some form of overall charge neutrality is maintained. Thus a double negative ion is often compensated by the presence of a double positive ion or more likely by near by negative ion vacancy. We allow for this as well. In this case we consider a negative ion vacancy in one of three places: a) in a



shell third neighbor to the  $\text{NH}_4^+$  ion labeled (7,7-7) b) in a shell fifth neighbor to the  $\text{NH}_4^+$  ion labeled (0,7-14) c) in the first shell to the  $\text{NH}_4^+$  ion labeled (0,7,0). This is seen in the final figure labeled  $\text{NH}_4^+$  5x5x5 array. This array is neutral and consists of two types a perfect crystal which duplicates the results of the first figure and is called D=0, and the double negative ion with associated charge compensation. As is seen the charge compensation only weakly modifies the effect on  $\text{H}^+$  removal. We conclude negative charged regions promote the availability of H or  $\text{H}^+$  ions for further chemical reaction. Furthermore the removal of the  $\text{H}^+$  leaves a neutral  $\text{NH}_3$  behind which in the lattice looks like a net negative region to a neighboring  $\text{NH}_4^+$  ion. The ingredients for a chain reaction of sorts may be present. Currently we are completing like studies for the  $\text{ClO}_4^-$  ion.

#### Molecular Crystal-ICECAP (MC-ICECAP)

The general procedure called ICECAP has been described fully at a prior time. The procedure which is an Acronym for I(onic) C(rystal) E(lectronic) C(alculation) A(utomated) P(rogram) has been given a reasonably general recent implementation. This implementation is tuned to systems which are bulk in nature and which have relatively simple unit cells. This tuning is optimal for most ionic type crystals including ceramics, but is rather less than optimal for a Van der Waals type of system, such as nitro-methane or RDX for that matter. The flaw is in the particular ICECAP implementation would the process itself. Basically, the given implementation would work reasonably well for

complex systems, in terms of precision, but would be hopelessly slow in the general application.

To rectify these problems, a new form of ICECAP which we call MC-ICECAP has been formulated. The nomenclature refers to the essential modifications to the basic ICECAP procedure to tune it to the essential features of a Van der Waals bonded system. There are two basic assumptions made here. The first is that there is some finite distance away from some possible lattice flaw, for which the molecules comprising the system look the same as the molecules in the pure, perfect, periodic lattice. They may not be sited at the perfect lattice site, that is fine, and they may be polarized a small amount, as long as the polarization is described by linear response theory. These molecules are said to comprise the environment. The remaining molecules termed the cluster, need not be governed by linear response theory. The second assumption, and the one not made in normal ICECAP is that the molecules in a Van der Waals system overlap only a very small amount. The key ingredient in this assumption is that the local orbital screened potential is given in terms of inter-molecular coulomb potentials alone. These may be of a polarization type.

The essential virtue of the approach about to be described is that, the complexity of a problem viewed in the usual band theory (or molecular orbital) way is significantly reduced. Consider a normal MO picture of a molecule consisting of  $N$  atoms, each with  $n$  electrons. If one uses Hartree-Fock theory and second order perturbation theory, then the time to do the calculation scales as  $(Nn)^5$ , and the disc storage scales as  $(Nn)^4$ . If the local orbital translation applies and is made, the time factor reduces to  $N(n)^5$ ,

and the disc storage scales as  $(Nn)^{4+}(Nn)^2$ . These potential savings are significant. For example in a solid such as  $N_2O_2$  which has two  $N_2O_2$  units per unit cell, one need at most consider two separate but connected  $N_2O_2$  units independently, rather than a cell of  $2(N_2O_2)$  units.

As an example, consider a molecular solid. Assume that the molecular orbitals for the pure, perfect, periodic solid are known. Consider initially that the system consists of an environment and a cluster of a single molecule. This restriction will be removed later. The potential due to the environment is given in terms of the potentials of the ions at each site  $N$  as:

$$V(\vec{R}_N) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} A_{\ell}^m Y_{\ell}^m r^{-\ell-1} + \sum_{m=-1}^1 I_1^m Y_1^m r^{-2} \quad (1)$$

The coefficients  $A$  refer to the intrinsic potential of the environmental molecule, whereas the coefficients  $I$  refer to the induced dipole moments. Thus each molecule is represented as a simple 1-body potential of a complicated form. The other molecule, called the cluster here is said to be a site  $a$ . The equation satisfied by the HF system for the molecules at site  $a$  is a simply:

$$[F_A + \sum_{n \neq A} V(\vec{R}_N)] \phi = \epsilon \phi \quad (2)$$

This equation which is often used by cluster modellers is incomplete, and neglects the orthogonalization terms due to other electronic orbitals. This has been known since the pioneering work of Adams and Gilbert in the early 1960's. More appropriately, one needs the Adams-Gilbert equation to describe the embedded cluster. This is in its full generality:

$$[F_A + \sum_{N \neq A} V(\vec{R}_N) - \rho_A] \hat{\phi} = \hat{\epsilon} \hat{\phi} \quad (3)$$

However Kunz has shown (1969) that for systems with small overlap this reduces to a simpler equation. This is the Adams-Gilbert-Kunz equation:

$$[F_A + \sum_{N \neq A} V(\vec{R}_N) - \rho_A \sum_{N \neq A} V(\vec{R}_N) \rho_A] \hat{\phi} = \hat{\epsilon} \hat{\phi} \quad (4)$$

It is this equation which we will use for MC-ICECAP.

To proceed consider a normal quantum chemical solution method. Expand the solution to the A-G-K equation in a basis of  $X_i$ 's.

First one sees

$$A_{ij} = \langle x_i | F_A + \sum_{N \neq A} V(\vec{R}_N) - \rho_A \sum_{N \neq A} V(\vec{R}_N) \rho_A | x_j \rangle \quad (5)$$

and

$$A_{ij} = \langle x_i | F_A | x_j \rangle + \langle x_i | \sum_{N \neq A} V(\vec{R}_N) | x_j \rangle - \sum_{\ell} \sum_m \langle x_i | \hat{\phi}_{\ell} \rangle \langle \hat{\phi}_{\ell} | \sum_{N \neq A} V(\vec{R}_N) | \hat{\phi}_m \rangle \langle \hat{\phi}_m | x_j \rangle$$

But, one extracts the ordinary Fock matrix here. That is

$$F_{ij} = \langle x_i | F_A | x_j \rangle$$

and also define the external potential matrix:

$$V_{ij} = \langle x_i | \sum_{N \neq A} V(\vec{R}_N) | x_j \rangle$$

This yields

$$A_{ij} = F_{ij} + V_{ij} - \sum_{\ell} \sum_m \langle x_i | \hat{\phi}_{\ell} \rangle \langle \hat{\phi}_{\ell} | \sum_{N \neq A} V(\vec{R}_N) | \hat{\phi}_m \rangle \langle \hat{\phi}_m | x_j \rangle \quad (6)$$

Define:  $\hat{\phi}_n = \sum_o C_o^n x_o$ ;  $S_{pq} = \langle x_p | x_q \rangle$

$$\langle x_i | \hat{\phi}_i \rangle = \sum_p C_p^1 S_{ip}$$

So that finally:

$$A_{ij} = F_{ij} + V_{ij} - \sum_{\ell} \sum_m (\sum_p C_p^1 S_{ip}) (\sum_q C_q^m S_{qj}) (\sum_r C_r^1 \sum_s C_s^m V_{rs}) \quad (7)$$

It is this equation that one solves.

The extension of this to more complex clusters is trivial. One has a separate A-G-K equation for each molecule unit in the cluster (hence the scaling in time and storage as  $N$ ). The

external potential seen by each cluster molecule includes terms now from the other  $N-1$  cluster molecules as well as the environment, but otherwise the equations solved remain unchanged.

As an illustration to this set of equations consider a simple lattice vacancy. The molecules neighboring the vacancy in the first shell of neighbors may well be alike to each other but different from the ones in the second shell, which are alike to each other, and in turn all of these are not exactly the same as the molecules at larger distance, which resemble the pure, perfect, periodic lattice molecules. Thus for instance in a simple fcc solid (such as Kr) one has a vacancy at (000), the first shell of surrounding atoms at (110) etc. and the second shell at (200) etc. The bulk like atoms begin at (211) etc. shell. There is no atom at (000), 12 at (110), 6 at (200), and infinite number beyond. Nevertheless the essential physics requires here that we understand only 3 atoms. The coupled A-G-K equations yield these answers as advertised. The remaining solutions are obtained by use of symmetry. This is being coded for large complex molecules now. The computer of choice for this is the FPS T-40 supercomputer available in our laboratory. This machine has recently produced speeds in excess of 273 million floating point operations per second in our tests, and is ideal in speed and architecture for these problems. However, even with the speed available, without the A-G-K process here described the study of a defect complex in RDX would be impossible in our view.

Annual Report  
N00014-86-K-0149

NMR Imaging Lab

I. Summary

Since the installation of the 85kG superconducting magnet in the summer of 1986 a complete NMR imaging spectrometer has been constructed and used to produce research quality NMR spectra and images. Preliminary tests have been made on a high power sinusoidal gradient imaging system with some positive results. Spectrometer development is performed jointly under this contract and under ONR contract N00014-86-C-0724 subcontract SK80D7820F.

Preliminary measurements have been made using  $\text{NaClO}_3$  which undergoes a thermal decomposition (1). Some measurements have been made on the feasibility of creating defects mechanically in alkali halides.

II. Details

A. Spectrometer Development

1. Hardware

The spectrometer is constructed using commercially available building blocks interfaced to a small computer. The equipment constructed locally from scratch includes IEEE-488 (GPIB) interface circuits, a pulse sequence generator, an oscilloscope display unit, and a digital input unit. The latter is the most recent addition and will be principally used to facilitate interactive processing of the raw NMR data. Three NMR imaging probes have been constructed. The third uses the main body of the first but has a new sample mounting arrangement and a new set of gradient coils. At present both existing probes are capable of static gradient techniques. One of them is also capable of dynamic gradient techniques though problems with the spectrometer itself have made attempts at such measurements unsuccessful. We are

currently tracking down the problems in the dynamic gradient equipment.

New construction to install conditioned, isolated ground receptacles and a ground bus is complete. This improvement in the electrical system will aid in data collection by reducing interference from signals on the building ground associated with normal building operations.

A new intermediate frequency system will be installed in the near future to facilitate some line narrowing NMR pulse sequences which may lead to increased image resolution.

## 2. Software

The software consists of five basic parts: control of the pulse sequence generator and hence the experiment to be performed, the acquisition of data with signal averaging, processing of accumulated data, the creation of an NMR image from a set of data, and modest processing of images.

Most of the software is written in fortran with interfacing and time critical portions in assembly language.

## B. Proofing the Spectrometer

NMR spectra have been obtained for  $^6\text{Li}$  and  $^7\text{Li}$  in an aqueous solution and in an AlCuLi alloy,  $^{23}\text{Na}$  spectra have been obtained in an aqueous NaCl solution and NaCl and  $\text{NaClO}_3$  solid samples. Metallic aluminum filings were measured using the  $^{27}\text{Al}$  resonance both before and after annealing. NMR images have been obtained using the static gradient technique and the  $^{23}\text{Na}$  signal from both powdered NaCl inhomogeneously distributed on a microscope slide and single crystals of  $\text{NaClO}_3$ . In the latter case the NMR line is split by internal electric quadrupole fields and the image is made using one of the satellites. This will result in an image which is quite sensitive to local lattice distortions. Measurements using the sinusoidal gradient technique using salt water achieved a gradient field strength of roughly 50 gauss/cm without significant difficulties (this will be improved with new coils under development). The use of the sinusoidal gradient

technique to obtain research quality images has been thwarted by problems within the spectrometer. We suspect that it is a triggering problem in the sinewave generator circuitry.

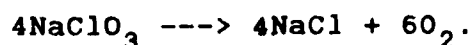
## C. Specific Results

### 1. General

We have undertaken the study of defect formation in NaCl, KBr, and NaClO<sub>3</sub>. The defects are formed in the alkali halides mechanically whereas we use the defects created during thermal decomposition in the case of NaClO<sub>3</sub>. For NaCl and NaClO<sub>3</sub> we can easily observe the sodium NMR signal, whereas in KBr we monitor the bromine signal. Signals can be obtained from chlorine and potassium though they will be weak.

### 2. Sodium Chlorate

Samples of single crystals of NaClO<sub>3</sub> have been grown from an aqueous solution. These crystals will have an NaCl type structure with some distortion to accommodate the chlorate group (1,2). Upon heating above 100°C the samples lose mass as the material begins to decompose. The decomposition follows the general form



It is unclear at present exactly how the intermediate steps proceed. It is hoped that theoretical work under this program will help to understand the process in more detail. There is evidence in the literature to suggest that the decomposition occurs first in regions of high stress (1). We have measured for one sample, ground to a coarse powder, oxygen evolution using a mass spectrometer. These results are shown in figure 1. Initially air and hydrocarbon contaminants (fingerprints, vacuum pump oil) are seen. However as time progresses and the temperature increases, a steady evolution of oxygen is observed which appears to



emerge in bursts. This type of behavior is very reminiscent of the fracto-emission work of Dickenson, et al (3). After the initial few minutes no sodium or chlorine evolution is observed. We have also measured the optical absorption (190nm to 820nm wavelength) of a sample for possible comparison with future theoretical work. The absorption shows an excitonic peak typical of simple solids with a maximum at a wavelength of 210 nm (5.9 eV).

Imaging experiments were performed using  $\text{NaClO}_3$  before and after heating. The images which resulted were highly distorted and uninterpretable. Some examination showed that this was predominantly due to changes in the NMR spectrum with sample heating by the gradient coils. We have examined this behavior in a non-imaging mode. Two of the resulting spectra are shown in figure 2 which illustrate the changes in the spectra with temperature. These spectra were obtained with the magnetic field oriented near a cubic axis. There are two major changes with temperature, the overall splitting due to the internal electric quadrupole field is seen to decrease with temperature and the outer ("satellite") peaks become broader. These changes are reversible and so are not directly associated with defect formation but a careful study may help to understand the underlying microscopic changes in the unit cell and hence provide clues as to the decomposition pathway. We plan to investigate this further in the near future. One principle feature will be to investigate whether the line broadening is the same for all nuclei (homogeneous) or represents a distribution of effects over the sample (inhomogeneous) perhaps due to differing degrees of stress or strain within the sample. We will carry these experiments to significantly higher temperatures under more controlled conditions. Only one previous Na NMR study has been found which measures temperature effects (4) and then to only 63°C.

New circuitry has been added to the spectrometer to turn off the gradient coils between measurements and hence

allow large gradients with little heat generation.  
Preliminary images show substantial improvements (fig. 3).

### 3. NaCl and KBr

Commercially available crystals of NaCl and KBr have been acquired. Preliminary tests with a drop hammer constructed locally show that initially clear samples can be made cloudy when hit with the hammer. Some experimentation was done to determine the correct height for the hammer to avoid breaking the samples. It is likely that the cloudiness is due to microcracks formed in the sample. As of this date we have not performed any conclusive NMR measurements using these samples.

## NMR Lab - References

- (1) I. D. Begg, P. J. Halfpenney, R. M. Hooper, R. S. Narang, K. J. Roberts, and J. N. Sherwood, Proc. R. Soc. Lond. A 386 431 (1983).
- (2) R. W. G. Wyckoff, Crystal Structures, 2nd ed., Vol. 2, page 380 (Wiley & Sons 1964).
- (3) J. T. Dickenson, S. C. Langford, L. C. Jensen, G. L. McVay, J. F. Kelso, C. G. Pantano, "Fracto emission from fused silica and sodium silicate glasses", J. Vac. Sci. Technol., in press.
- (4) H. S. Gutowsky and G. A. Williams, Phys. Rev. 105, 464 (1957).

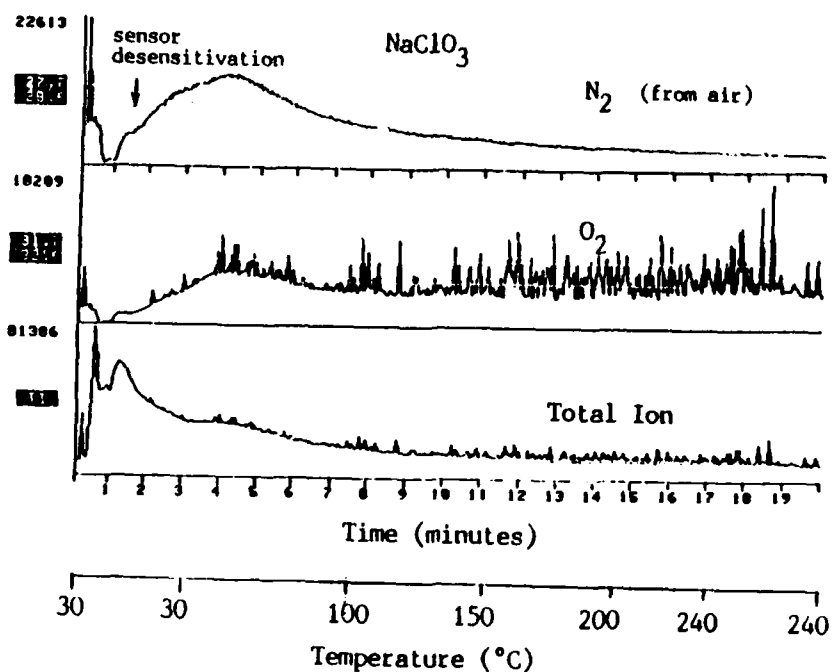


Figure 1 - Summary of mass spectrum analysis of decomposition of Sodium Chlorate.

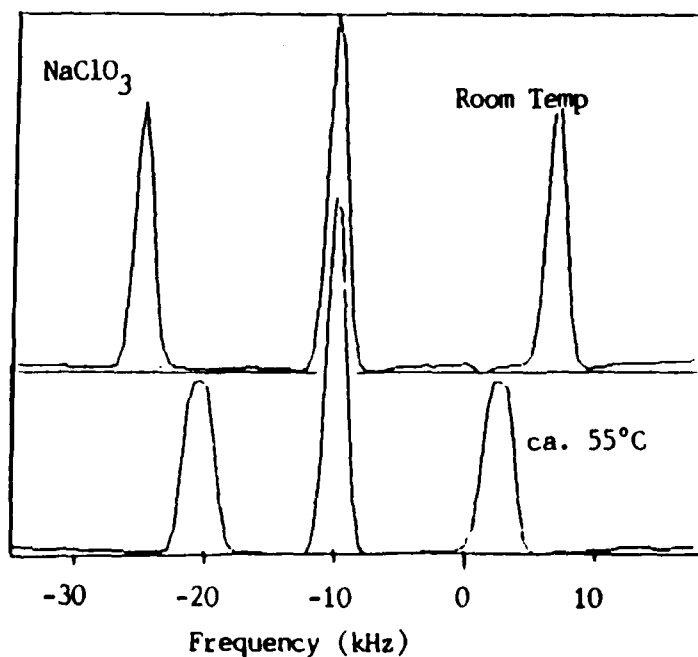


Figure 2 - NMR spectra of  $\text{NaClO}_3$  showing the change in the quadrupole splitting and the broadening of the quadrupole satellites as the temperature is raised. The zero of the frequency shift corresponds to 95.18MHz.

$\text{NaClO}_3$   
9.65 x 9.15 x 2.6mm

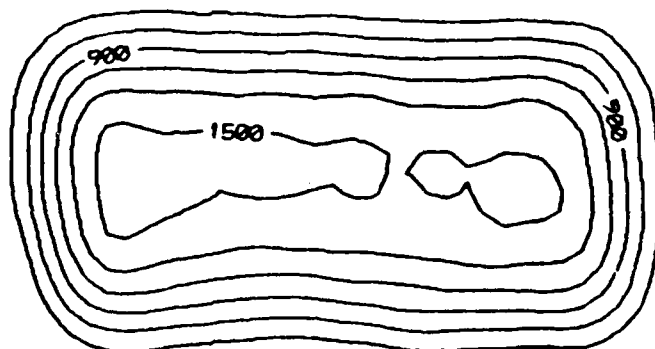


Figure 3 - NMR image of Sodium Chlorate sample. Sample is oriented  $53^\circ$  from perpendicular to the magnetic field to maximize the separation between the satellites and the central peak. In this image, the axis of rotation is in the horizontal direction.

## Summary of Research Activities - B. H. Suits

### Presentations

"Spatially Resolved NMR Spectra using Periodic Magnetic Field Gradients", March 1987 Meeting of American Physical Society, New York.

"Prospects of NMR Imaging in Processing Rheology as Related to Propellant Manufacture" with J. C. Crowley (Lockheed), Workshop on Dynamic Deformation, Fracture and Transient Combustion, May 1987, Great Oaks Landing, MD.

"NMR Imaging of Solids", seminar, U. S. Army Technology Lab, Watertown, Mass, August 1987, P. Sagalyn sponsor.

### Publications

"A nuclear magnetic resonance study of Al-Mn quasicrystals and related materials" K. R. Carduner, B. H. Suits, J. A. Diverdi, M. D. Murphy and D. White, J. Mater. Res. 2, 431 (1987).

"Imaging electromagnetic fields using the magnetic resonance absorption spectrum of a paramagnetic gas" S. A. Marshall, B. H. Suits, M. T. Umlor and Y. N. Zhang, J. Magn. Reson. 76, in press (1988).

"An NMR Study of Li in AlLiCu Icosahedral Alloys", Cheol Lee, D. White, B. H. Suits, P. A. Bancel, and P. A. Heiney, Phys. Rev. B, accepted Jan. 1988.

Report on ESR Laboratory Work Performed for the oNR Contract.  
(S. A. Marshall)

During the course of this reporting period, a number of problems were initiated, all of which dealt with the nature of defects in solids. These problems were selected partly because of their basic scientific interest and partly because of their potential in having their magnetic species used as labels for magnetic resonance imaging.

Before proceeding however it should be mentioned that some trials were made on systems initially considered to be appropriate to the general area of energetic materials. Of these, one was determined to be appropriate to the long term goals of the project in that it experimentally established the notion of stress generated paramagnetic species in an otherwise non-magnetic medium. The system in question was high purity fused quartz does not exhibit a significant ESR spectrum. That is, the concentration of free radical species or broken bonds seems minimal. Subsequent gamma-irradiation of this medium produces strong ESR signals suggesting that broken bonds are produced by the high energy photons. This of course is by no means surprising in view of the work done over the past three decades on radiation produced defect species in condensed media. What is observed is the following. When annealed, high purity quartz is crushed into a fine powder, an ESR spectrum is observed which is otherwise not observed and which is in many respects similar to the spectrum observed in the gamma-irradiated medium. This is believed to be an effect which is not isolated to quartz or to quartz-like media but may very well be one which takes place in various solids. The reason it is so readily observed in high purity quartz and not so in other media may be due to (a) the purity of the medium, (b) its thermal stability, and (c) the narrowness of its ESR spectral component lines which are of the order of 0.5 Oersteds which in turn are so because of the fact that fused quartz is a solid whose atoms are composed of the nuclei, oxygen (16) and silicon (28), which have zero magnetic moments. It is suggested that work along these lines be continued in view of its potential relevance to the

study of instabilities of energetic materials to mechanical stress.

In another area, that of the response of single crystals of magnesium oxide (periclase) to mechanical stress, a study due to J. T. Dickinson, L. C. Jensen, and M. R. McKay has shown that in some specific "cloudy" specimens of magnesium oxide, the fracture induced emission of gases was found to be significantly higher than in "clear" specimens of this material. In view of these results, we have undertaken an ESR study of both "clear" (Norton Company) MgO and "cloudy" (Super Refractories) MgO. The abbreviated results and conclusions of our study on these two specimens of magnesium oxide are a result of evaluations of the spectrum of the divalent manganese ion impurities. Both crystals exhibit the spectrum of divalent manganese which nominally consists of thirty allowed lines. Furthermore, we find for both crystals, that the manganese ESR spectra yield identical data on the ion's magnetic moment, its nuclear hyperfine interaction energy as well as on its cubic crystalline electric field energy. However, the two crystals demonstrate some unusual differences. For one, the  $M = +1/2$  to  $+3/2$  transitions, although observable, were much broader than those in the "clear" crystals. Our interpretation of these observations is that in both the "cloudy" and "clear" crystals, a mosaic effect is operating and that in the "cloudy" specimen it far exceeds the effect which takes place in the "clear" specimen. From our preliminary studies we have been able to identify as well as quantified this effect. We find that in the "cloudy" MgO specimen there exists a mid-range disordering that takes the form of a mosaic structure whose Gaussian width is 5.0 degrees-of-arc and whose crystalline electric field amplitude is uncertain by about 1.0 per cent while in the "clear" specimen, the mosaic width is under 0.50 degree-of-arc and its crystalline electric field uncertainty is of the order of 0.1 per cent. We therefore conclude that the two crystals are basically the same except that in one, the "cloudy" crystal, there exists a disorder which has a significant effect upon spectral line widths but on average leaves spectral components unaffected. In an effort to understand the problem a bit more fully, an electron microscopy



study of these two crystals was undertaken by an under graduate student of the MTU's physics department. This study proved to be very informative in that it demonstrated a possible source of this disorder. This microscopy study, although as yet incomplete, demonstrates the existence of voids in the "cloudy" specimen. (In fact, no evidence of voids in the "clear" magnesium oxide could be detected from the electron microscopy photographs.) These voids are identified as gaseous inclusions trapped perhaps during the arc-fusion growth process.

A third study undertaken during the course of this year's effort was that of the superhyperfine structure spectrum of the divalent manganese ion in single crystal zinc selenide having the zinc blende phase. The object of this study was to determine how nearly perfect a single crystal could be obtained of a II-VI compound and to then study the ESR spectrum of a paramagnetic impurity, say divalent manganese, before and after stresses of various kinds are applied. We have completed the first phase of this work and have measured with some precision the following: (a) the self hyperfine structure energy of manganese (55), (b) the first shell superhyperfine structure (SHFS) energies of the selenium (77) ion, (c) the second shell SHFS energies of zinc (67), and finally the third shell SHFS energies of selenium (77). This is a rich spectrum and should be capable of being used to provide information of the nature and degree of disorder introduced by various stresses.

During the course of this one year's effort, two oral papers were presented, one at the Rocky Mountain Magnetic Resonance Symposium held in Denver, Colorado on Imaging of Electromagnetic Fields in Microwave Resonators, and one at the 1987 Midwest Solid State Conference held in Notre Dame University, Norte Dame, Indiana on The Superhyperfine STructure Spectrum of Divalent manganese in Single Crystal Zinc Selenide. In addition two papers were submitted and accepted for publication in 1988, one on Angular Momentum Operator Equivalents and one on Imaging of Electromagnetic Fields in Microwave Resonators. Further, one paper has been submitted for publication on The ESR Spectrum of Tetravalent Chromium in Single Crystal Alfa-Alumina. Also, two

papers which bear upon the work performed on this contract are currently being drafted for future publication. These deal with the ESR spectra of manganese in "cloudy" and "Clear" magnesium oxide and another on manganese in zinc selenide.

Finally, one graduate student, Mr. M. T. Umlor, received the Master of Science degree in physics and wrote a thesis on work performed during the course of this contract. It should also be noted that the following people made contributions to this research effort: G. Dace, and MTU undergraduate, C. Lai, Y. N. Zhang, M. T. Umlor, all MTU graduate students, Professor D. Yoder-Short of MTU and Professor J. Furdyna of Nortre Dame University.

A. Barry Kunz  
Professional History

Dr. A. Barry Kunz was born in Philadelphia, Pennsylvania, October 2, 1940, to Commander and Mrs. Albert Kunz. He received his early education in the Allentown, Pennsylvania Public School System. He received his B.S. degree cum laude in physics from Muhlenberg College in 1962. He entered Lehigh University in the fall of 1962 to pursue graduate studies in physics. He received his M.S. Degree in January 1964 and his Ph.D. in June 1966. His graduate studies were aided by a graduate fellowship from NASA. From 1966 to 1969 he remained at Lehigh University as an instructor in physics and research associate on projects supported by the Atomic Energy Commission and the Air Force Office of Scientific Research. In September 1969 he became a Research Assistant Professor of Physics at the University of Illinois at Urbana-Champaign and a member of the Materials Research Laboratory. He received several promotions including that to Professor of Physics in 1976, a post he held until August 1984. During the period 1971-1974 he was employed part-time by the Solid State Section of the Aerospace Research Laboratory, WPAFB, in Dayton, Ohio as a research analyst. In 1973 he was co-director of the NATO Advanced Study Institute on "Elementary Excitations" in Antwerp, Belgium. He was a consultant to the photoproducts division of E. J. Dupont, Inc. from 1974-1979. He has had an appointment to the AFOSR, physics research evaluation group. During the calendar year 1981 he was visiting professor at MTU. Currently he is Presidential Professor of Physics at Michigan

Technological University and head of the Physics Department. In 1981 he organized the "Frontiers of Physics Symposium" at MTU, which included Nobel Laureate, Willis Lamb and Buckley Laureate, Albert Overhauser among the speakers. He has served on several organizing committees for the Sanibel Symposia organized by the University of Florida. He maintains working relationships with several organizations external to UIUC or MTU. These include S. B. Trickey and R. Bartlett at the University of Florida, J. M. Kauffman at the Johns Hopkins University, and C. P. Flynn at the University of Illinois.

He is a consultant to Los Alamos National Laboratory and to Energetics, Inc. In 1986 he was awarded the MTU distinguished research award and in 1987 the Michigan Universities Board of Governor's outstanding faculty award. He serves on the editorial board of the International Journal of Quantum Chemistry and of Computers in Physics. He is a Fellow of the American Physical Society, a member of Sigma Xi, Phi Alpha Theta and Sigma Pi Sigma honorary societies.

He has been a pioneer in the implementation of Hartree-Fock crystal code and results ( $\text{LiCl}$ ). In 1971 he extended the electronic polaron method to whole states which allowed accurate band calculations for insulating solids for the first time. This culminated in 1973 in a theory of core state absorption of x-rays by insulators including exciton and multiple exciton formation. In the period 1975 to 1980 he was a leader in rigorous implementation of cluster techniques for condensed matter systems. Since 1981 he had been active in including rigorous quantum

chemical methods to correlate solid state calculations both in the cluster or the infinite solid mode. These have produced useful and sometimes startling results for diverse systems such as solid CH<sub>4</sub> and pure or defective metals. Currently, he is fostering research collaboration between MTU, the University of Manitoba and Harwell AERE, England, on self-consistent methods for studies of charged defects in non-metallic solids.

A. Barry Kunz  
Administrative Experience

In addition to remaining active in research and teaching, beginning in 1980 Dr. Kunz has served as a consultant to the Dean of Sciences and Arts of Michigan Technological University, Houghton, Michigan. In 1983, 1984, 1985 and 1986 he organized a Great Lakes Summer Research Workshop at MTU in Condensed Matter Physics. In 1984 a panel was organized and chaired for the U.S. Department of Energy on Theory and Simulation of Materials Structures. During his period as Head of the Physics department, he has had the annual departmental research funding rise by a factor of 10 (from \$80,000/year to \$1,000,000/year). The faculty has increased from 16 to 23, the graduate population from 3 to 30, and a Ph.D. program in Applied Physics is being implemented. He is active in fostering interdisciplinary programs and has founded along with the departments of Mathematics and Computer Science, the Center for Experimental Computation which is heavily involved in research into parallel computing. He is also currently active in fostering interdisciplinary research into Materials by Design.

### Education

B.S., Physics, Muhlenberg College, Allentown, 1962.  
M.S., Physics, Lehigh University, Bethlehem, 1964.  
Ph.D., Physics, Lehigh University, Bethlehem, 1966.

### Experience

1987 - Present: Consultant, Los Alamos National Laboratory  
1986 - Present: Consultant, Energetics, Inc.  
1984 - Present: Presidential Professor, Head, Physics, Michigan Technological University.  
1976 - 1984: Professor, Physics, University of Illinois Urbana Champaign.  
1982 - 1984: Adjunct Professor, Physics, Michigan Technological University.  
1982 - Present: Director, Institute for Condensed Matter Studies, Michigan Technological University.  
1973 - 1976: Associate Professor, University of Illinois, Urbana.  
1974 - 1979: Consultant, Photo Products, E. J. Dupont.  
1971 - 1973: Assistant Professor, University of Illinois, Urbana.  
1971 - 1974: Research Analyst, U.S. Air Force Aerospace Research Laboratory, WPAFB, Dayton.  
1969 - 1971: Research Assistant Professor, Physics and Materials University of Illinois, Urbana.  
1966 - 1969: Research Associate and Instructor, Lehigh University, Bethlehem.

### Honors

1987: Editorial Board Computers in Physics  
1987: Michigan Universities Board of Governors Outstanding Faculty award  
1986: MTU Distinguished Research Award  
1985: Editorial Board International Journal of Quantum Chemistry  
1984: Chairman, U.S. Department of Energy, Panel on Theory and Simulation of Defects  
1976: Elected Fellow of the American Physical Society

## Technical Topics of Expertise

Computer Modeling  
Catalysis, Bonded Catalysts  
Surface Science, Surface Defects, Chemisorption  
Ionic Solids, Molecular Solids, Energetic Solids  
Defects in Metals

### A.B. KUNZ - Publications, 1980 to present.

119. D. C. Reynolds, R. J. Almassy, C. W. Litton, G. Koos, A. B. Kunz and T. C. Collins. Donor-Acceptor Recombination Spectra in CuCl. Phys. Rev. Lett. 44, 204 (1980).
120. G. C. Wepfer, G. T. Surratt, R. S. Weidman and A. B. Kunz. Theoretical Study of H Chemisorption on NiO, II. Surface and Second-Layer Defects. Phys. Rev. B 21, 2596 (1980).
121. A. B. Kunz and D. M. Ginsberg. Band Calculations of the Effect of Magnetic Impurity Atoms on the Properties of Superconductors. Phys. Rev. B 22, 3165-3172 (1980).
122. A. K. Ray, S. B. Trickey, R. S. Weidman and A. B. Kunz. Lattice Constant at the Insulator-Metal Transition of Crystalline Xenon. Phys. Rev. Lett. 45, 933-935 (1980).
123. A. B. Kunz, R. S. Weidman, J. Boettger, and G. Cochran. Theory of Electronic States in Narrow-Band Materials; Applications to Solid Ar, CuCl and CdS. Int. J. Quant. Chem. S 14, 585-596 (1980).
124. H. Itoh, G. Ertly and A. B. Kunz. Molecular Orbital Study on the Interaction of Single-Transition Metal Atoms with NH<sub>3</sub> and H<sub>2</sub>O Ligands, Z. Naturforsch. 36 a, 347-353 (1981).
125. A. B. Kunz and T. O. Woodruff. Some Highly Excited States of the LiH Molecule: Calculations Relevant to Core-Hole Initiated Relaxation Processes (CHIRP's) in Ionic Crystals, Sol. St. Comm. 38, 629-631 (1981).
126. K. L. Bedford and A. B. Kunz, Ab Initio Studies of the Electronic Properties of the Silica Surface, Sol. St. Comm. 38, 411-414 (1981).
127. A. B. Kunz and J. T. Waber. Positron and Electron Energy Bands in Several Ionic Crystals Using Restricted Hartree-Fock Method. Solid ST. Commun. 39, 831-834 (1981).
128. A. B. Kunz, R. S. Weidman and T. C. Collins. Pressure Induced Modifications of the Energy Band Structure of Crystalline CdS. J. Phys. C 14, L581-L584 (1981).



129. H. Itoh, G. Ertl and A. B. Kunz. A Molecular Orbital Study on the Interaction of Dinitrogen with Transition Metal Atoms. *Chemical Physics* **59**, 149-156 (1981).
130. A. B. Kunz, Electronic Structure of NiO. *J. Phys. C* **14**, L455-L460, (1981).
131. R. S. Weidman, K. L. Bedford and A. B. Kunz. Ab Initio Calculations of the Electronic Properties of Polyethylene, *Sol. St. Commun.* **39**, 917-919 (1981).
132. A. B. Kunz, Properties of Narrow Band Insulators, *Int. J. Quant. Chem.* **515**, 487-498 (1981).
133. J. M. Blaisdell and A. B. Kunz. Theoretical Study of O Chemisorption on NiO. *Solid St. Commun.* **40**, 745-747 (1981).
134. A. K. Ray, S. B. Trickey and A. B. Kunz. BDD - FCC Allotropy, F-Bands and Metallization in Xe and Kr. *Solid ST. Commun.* **41**, 351-353 (1982).
135. K. L. Bedford and A. B. Kunz. Ab Initio Studies of the Initial Adsorption of Oxygen onto the Aluminum (100) Surface. *Phys. Rev. B* **25**, 2119-2123 (1982).
136. L. A. Grunes, R. D. Leapman, C. N. Wilker, R. Hoffmann, and A. B. Kunz. Oxygen K near-edge Fine Structure: An Electron-energy Loss Investigation with Comparison to New Theory for Selected 3d Transition-metal Oxides. *Phys. Rev. B* **25**, 7157-7173 (1982).
137. A. B. Kunz. Study of the Electronic Structure of Twelve Alkali-Halide Crystals. *Phys. Rev. B* **26**, 2056-2069 (1982).
138. A. B. Kunz. Electronic Structure of AgF, AgCl and AgBr. *Phys. Rev. B* **26**, 2070-2075 (1982).
139. A. D. Zdetsis and A. B. Kunz, Cluster Adsorption of Argon on Alumina. *Phys. Rev B* **26**, 4756-4758 (1982).
140. A. B. Kunz and J. T. Waber, Concerning the Trapping of Positrons in Ionic Solids, in Positron Annihilation, P. G. Coleman, S. C. Sharma and L. M. Diana, Eds., 682-683 (North-Holland, 1982).
141. A. Y. S. Kung, A. B. Kunz and J. M. Vail, Unrestricted Hartree-Fock Cluster Analysis of F and F<sup>-</sup> Centers in some Alkali Halides. *Phys. Rev. B* **26**, 3352-3360 (1982).
142. C. E. Brion, I. E. McCarthy, I. H. Suzuki, E. Weigold, G. R. J. Williams, K. L. Bedford, A. B. Kunz and R. S. Weidman, Electron Momentum Distributions and Binding Energies for the Valence Orbitals of Hydrogen Bromide and Hydrogen Iodide. *J. of Elect. Spect. and Rel. Phenom.* **27**, 83-107 (1982).

143. G. S. Handler and A. B. Kunz, The Self-Energy of a Free Electron Gas. Chem. Phys. Lett. 460-462 (1982).
144. A. B. Kunz and J. T. Waber, A Theoretical Study of the Binding of Positrons to Gaseous Molecules, in Positron Annihilation. P. G. Coleman, S. C. Sharma and L. M. Diana, Eds., 113-115 (North-Holland, 1982).
145. J. C. Boisvert, A. B. Kunz and T. O. Woodruff, Core Excitons in Ionic Crystals: I. A Born-Haber-type cycle for the energy of the Core Exciton Associated with the NaLII,III Edge in NaF. J. Phys. C. 15, 5033-5036 (1982).
146. A. B. Kunz, J. C. Boisvert and T. O. Woodruff, Core Excitons in Ionic Crystals: II. Calculations of the Na LII,III Edge in NaF. J. Phys. C. 15, 5037-5043 (1982).
147. A. B. Kunz and T. O. Woodruff, Core Excitons in Ionic Crystals: III. Calculations (including correlations) of Atomic Energies required in the Born-Haber Cycle for the Na LII,III Edge Exciton in NaF. J. Phys. C. 15, 5045-5047 (1982).
148. J. C. Boettger and A. B. Kunz, Ab Initio Energy Bands for CdO. Phys. Rev. B 27, 1359-1362 (1982).
149. A. B. Kunz and C. P. Flynn, A New Configuration Interaction Method for Excitons and Interband Processes Applied to LiF. J. Phys. C. 16, 1659-1663 (1983).
150. A. B. Kunz and C. P. Flynn, Excitonic Effects in the Interband Spectra of Metals. Phys. Rev. Lett. 50, 1524-1527 (1983).
151. Russian reprint of #117, updated for Soviet consumption (1983).
152. A. B. Kunz, Electronic Structure and Optical Properties of Solid Methane. Phys. Rev. B 28, 3465-3473 (1983).
153. J. M. Blaisdell and A. B. Kunz, "Theoretical Study of O Chemisorption on NiO, Perfect Surfaces and Cation Vacancies". Phys. Rev. B 29, 988-995 (1984).
154. A. B. Kunz, "A Series of Tests of Small and Medium Scale Computers Commonly Used for Computations by Solid State Theorists and Quantum Chemists". Int. J. Quant. Chem. Synp. 17, 623-627 (1983).
155. C. P. Flynn and A. B. Kunz, "Recent Results for Excitonic Processes in the Spectra of Metals and Alloys". Int. J. Quant. Chem. Synp. 17, 573-582 (1983).

156. A. K. Ray, S. B. Trickey and A. B. Kunz, "Optical Adsorption of Solid Xenon at High Pressure". *Phys. Stat. Sol. B* 121, K47-K50 (1984).
157. D. R. Beck and A. B. Kunz, "Excitation Energies for the Lowest Triplets and Singlet-triplet Splittings in Gas-phase Methane Including Many-body Effects". *J. Phys. B* 17, 2159-2168 (1984).
158. A. B. Kunz, "Theory of the Electronic Structure and Optical Properties of Organic Solids: Collective Effects", in Quantum Chemistry of Polymers, Solid State Aspects, ed. J. Ladik, 83-89 (D. Reidel 1984).
159. A. B. Kunz, "Chemisorption and the Electronic Structure of Transition Metal Oxides and Transition Metals Bonded to Oxide Surface". *Phil. Mag.* 51, 209 (1985).
160. A. B. Kunz, "Defect Simulations and Supercomputers". Reports on Materials Science, submitted.
161. A. B. Kunz, J. C. Boisvert and T. O. Woodruff, "LiK-edge Soft X-ray Absorption in LiF". *Phys. Rev.* B30, 2158 (1984).
162. M. H. Bakshi, G. A. Denton, C. P. Flynn, J. C. Boisvert, and A. B. Kunz, "Low-energy Excitonic Resonances in Metals I: Experiments on Divalent Atoms". *Phys. Rev. B*, Vol. 31, pp. 4972-4983.
163. J. C. Boisvert, P. W. Goalwin, A. B. Kunz, M. H. Bakshi, and C. P. Flynn, "Low-energy Excitonic Resources in Metals II: Cluster Calculation for Divalent Impurities in Li". *Phys. Rev. B*, Vol. 31, pp. 4984-4992.
164. A. B. Kunz, 1985, "The Electronic Structure of Impurities and Defects in Simple Metals". Characterization and Behavior of Materials with Submicron Dimensions, World Scientific Publishing Co.
165. A. B. Kunz, "Solid State Theory". The Encyclopedia of Physics, ed. Besancon.
166. A. B. Kunz, 1985, "Defect Simulation and Supercomputers." *Materials Science Forum*, Vol. 4, pp. 155-164.
167. M. H. Bakshi, G. A. Denton, C. P. Flynn, J. C. Boisvert and A. B. Kunz, "Low-Energy Excitonic Resonances in Metals, I. Experiments on Divalent Atoms", *Physical Review B*, Vol. 31, pp. 4972-4983. 1985.

168. J. C. Boisvert, P. W. Goalwin, A. B. Kunz, M. H. Bakshi and C. P. Flynn, "Low-Energy Excitonic Resonances in Metals, II. Cluster Calculations for Divalent Impurities in Li Metal", *Physical Review B.*, Vol. 31, pp. 4984-4992. 1985.
169. N. C. Bacalis and A. B. Kunz, 1985, "Ab Initio Calculations of Selected Ionization States of Cu on MgO" (001), *Physical Review B*, Vol. 32 pp. 4857-4865.
170. A. D. Zdetsis and A. B. Kunz, 1985, "Ab Initio Cluster Study of Ni Adsorption on Alumina", *Physical Review B*, Vol. 32, pp. 6358-6362.
171. A. B. Kunz, C. P. Flynn, J. C. Boisvert, M. Bakshi, "Electronic Structure of Impurities and Defects in Simple Metals, in Characterization and Behavior of Materials with Submicron Dimensions", World Scientific Publications, pp. 83-100, 1986.
172. A. B. Kunz, "Strategies of Studying Point Defects", Supercomputers, edited by F.A. Matsen and T. Tajima, University of Texas Press, pp. 250-268, 1986.
173. A. B. Kunz, "Computational Consideration in Solving the Many Electron Problem for Molecular System", Applications of Supercomputers, edited by D.F. Lockhart and D.L. Hicks, Journal of Applied Mathematics and Computation, pp. 23-33, 1986.
174. P. W. Goalwin, A. B. Kunz, "Perturbation-Theory Method of Calculating the Energies and Excitation Energies of Atomic, Molecular and Solid State Systems", *Physical Rev. B* 34, pp. 2140-2146, 1986.
175. P. W. Goalwin and A. B. Kunz, "Ab Initio Calculations of the Excitonic Spectra of the Alkali Halides Including Relativistic Effects", *Phys. Rev. B* 35, 5795 (1987).
176. A. B. Kunz, "Theoretical Study of Defects and Chemisorption by Oxide Surfaces, for Theory of Oxide Surfaces and Properties", J. Nowtny Ed., in press.
177. C. P. Flynn and A. B. Kunz, "Comment on Role of Electron-Hole Interactions in the Crystal Spectra of Metals", *Phys. Rev.*, in press.
178. A. B. Kunz, "A Cluster Model for the Adsorption of Rare Gas Atoms by Simple Metals", submitted.
179. A. B. Kunz and J. M. Vail, "Quantum Mechanical Cluster Lattice Interaction in Crystal Simulation", submitted.
180. A. B. Kunz and D. R. Beck, "Possible Role of Charged Defects in Molecular Solids", *Phys. Rev.*, in press.

181. A. B. Kunz, J. Meng and C. Woodward, "Computational Consideration for the Theoretical Study of Defects in Solid State Systems", submitted.
182. A. B. Kunz, "Embedded Cluster Method for Surface and Chemisorption Studies", submitted.

A. B. KUNZ - Invited Papers

- 1969 29 September to 4 October, European Congress on Molecular Spectroscopy, "Energy Band Structure and Optical Properties of Four Alkali Fluorides", Universite' de Liege, Belgium.
- 1972 4 July, International Conference on Electron Energy Structure, "Ab Initio Energy Band Studies for Ionic Solids", University of Exeter, England.
- 1973 18-30 June, NATO, Advanced Study Institute, On Elementary Excitation in Solids, Molecules and Atom. Two Lectures: "Ab Initio Energy Band Methods" "Soft X-ray Spectra of Molecules".
- 27-29 December, APS winter meeting at Berkeley, "Soft X-ray Spectra of Insulating Solids", University of Berkeley, California.
- 1974 January, International Symposium on Quantum Theory of Atoms, Molecules, and the Solid-State. "Many-Body Effects in Energy Band Theory", Sanibel Island, Florida (University of Florida).
- 22-26 July, IV International Conference on Vacuum Ultraviolet Radiation Physics, "Calculation of Optical Absorption Edges and Photo-Emission Edges in Solids", Hamburg, Germany.
- 17-18 November, Midwest Solid State Theory Symposium, "Photo-Emission Studies of Insulating Solids", Indiana University.
- December, Peat Symposium of the U.S. Geological Society, in cooperation with T. L. Phillips and D. J. Mickish, "Paleobotany of Petrified Peat (Coal Ball) Coal Member of the Illinois Basin", Miami Beach, Florida.
- 1975 23-27 June, Summer Research Conference in Theoretical Chemistry, Session Chairman on Subject of Ab Initio Theory of Crystal and Surface Science,\* Boulder, Colorado.
- 15 July to 15 September, "Centre European de Calcul Atomique et Maelculaire, Workshop on Ab-initio one-electron potentials". Seminar series declined, Orsay, France.
- 1976 18-24 January, International Symposium on the Quantum Theory of Atoms, Molecules and the Solid-State; Symposium Leader; Sanibel Island, Florida.
- 9-13 August, Gordon Conference on Atomic and Molecular Interactions.

- 1977 5 November, Midwest Solid State Theory Meeting, Argonne Nat. La., declined due to conflict.
- 1978 4-18 June, NATO ASI, Excited States in Quantum Chemistry, KOS, Greece.
- 1979 17 March, Int. Symp. on Quantum Chemistry, Electronic Properties of CuCl, Palm Coast, Florida.
- 25 August, Sagamore Conference on Crystallography, Mt. Tremblant, Canada.
- 1980 15 March, International Sym. on Quantum Chemistry, Recent Developments in CuCl and CdS, Palm Coast, Florida.
- 22 March, IBM Workshop on Effective One-Electron Potentials. Electronic Structure of Transition Metal Oxides, Ossining, New York.
- 1-4 July, Gordon Conference on Electron Distribution and Chemical Bonding - discussion leader.
- 1981 21 January, Workshop on Fundamental Research on Energetic Materials, Finite Cluster Techniques for Modeling Extended Systems, Berkeley, California.
- 14 March, International Symposium on Quantum Chemistry, Palm Coast, Florida. Fundamental Properties of Narrow Band Materials.
- June, Symposium of NRCC, Los Alamos. Two invited talks:
1. Simulation of Extended Systems by Finite Clusters
  2. Solid State Effective Potentials
- 1982 May, DOD Workshop on Energetic Materials: Properties of Energetic Solids and Molecular Crystals.
- 1983 12 March, Sanibel Symposium on Impact of Computers on Quantum Chemistry and Solid State Computations - Panel.
- 24 July - 5 August, "Excited States in Molecular Solids, Collective Effects", NATO ASI, Braunlage, West Germany on Quantum Theory of Polymers, Solid State Aspects.
- 9 August, "Energy Transfer, Trapping and Release in Molecular Crystals and Energetic Solids", DOD Workshop on Energetic Materials, Great Oaks, Maryland.
- 3 October, "The Electronic Structure of Impurities and Defects in Simple Metals", Fall Meeting of the Metallurgical Society and the American Society of Metals.
- 1984 1-10 March, Sanibel Symposium, Parts I and II, Organizing Committee for Part I and Session Chairman.

9-13 April, Royal Society of Chemistry, London, England;  
Invited Plenary Lecture: "Chemisorption and the Electronic  
Structure of Transition Metal Oxides and Transition Metals  
Bonded to Oxide Surfaces".

6-10 August, Department of Energy Panel on Simulation and  
Theory of Defect Structures in Solids ---, Chairman and  
organizer.

5-8 September, Midwest Solid State Theory Conference,  
Minneapolis, Minnesota, "Defect Simulation and Super  
Computers".

1985 17-20 March, High Speed Computers and the Future of  
Scientific Computation, University of Texas, Austin, TX  
"Theory of Defects and Supercomputers".

24-29 June, DoD workshop on Initiation Fundamentals, Great  
Oak, MD, "Defects in Energetic Solids".

5-6 August, Super Computer Conference, MTU, Houghton, MI,  
"Strategies For Studying Point Defects".

1986 29-31 January, DoD Workshop on Energetic Solids, Silver  
Spring, MD NSWC, "Defects and Initiation".

12-16 March, Sanibel Symposium, Marineland, FL, Session  
Chairman.

February 1986, D.O.E. Workshop on Energetics, White Oak,  
Maryland, "Mechanism for Destabilization of Energetic  
Solids".

October 1986, D.O.E. Conference on Initiation, Los Alamos,  
New Mexico.

1987 February 1987, FPS Symposium on Parallel Computer, "Computer  
Modeling of Solid State Defects", Dallas, Texas.

March 1987, Sanibel Symposium, "Computational Consideration  
for Solving the Many Body Problem in Solids", Marineland,  
Florida.

May 1987, DoD Workshop, "Theory of Defects in Energetic  
Solids", Great Oak, Maryland.

March 1987, APS March Meeting Pre Symposium, invitation  
declined due to conflict.

March 1987, DoD-DoE Symposium on Propellants, invitation  
declined due to conflict.



August 1987, Wright-Patterson Symposium on Advanced Computing, "Theory of Defects in Solids: Computational Strategies, Dayton, Ohio.

\*These sessions consist of a few short invited talks and an extemporized program.

Seminars given at the following:

National Bureau of Standards  
Aerospace Research Laboratory, Wright-Patterson AFB  
Brookhaven National Laboratory  
Argonne National Laboratory  
Oak Ridge National Laboratory  
Bell Telephone Laboratories (Murray Hill)  
Bell Telephone Laboratories (Holmdale)  
Eastman-Kodak Company  
E. I. Dupont de Nemours Company  
Belgian Atomic Energy Establishment-Mol  
University of Liege  
Lehigh University  
Drexel Institute of Technology  
Battelle Memorial Institute  
Queens College CUNY  
University of North Carolina  
Wake-Forrest University  
University of Georgia  
Stanford University  
Arizona State University  
Oklahoma State University  
University of Illinois  
Indiana University  
Purdue University  
Louisiana State University (Baton Rouge)  
University of Manitoba  
Texas A & M University  
Naval Research Laboratories  
U. S. Army Ballistics Research Laboratory, Aberdeen, Maryland  
Michigan State University  
Hirman College  
General Motors Corporation  
Michigan Technological University  
Air Force Avionics Laboratory  
University of Missouri, Columbia  
University of Missouri, St. Louis  
University of Missouri, Rolla  
Los Alamos National Laboratory  
University of New Orleans  
Johns Hopkins University  
University of Florida  
Western Kentucky University  
Washington State University  
Western Kentucky University

Washington State University  
Exxon Corporation, Clinton, NJ (seminar)  
Oak Ridge National Laboratory, NLTNIF  
Spokane, WA, APS Conference  
San Diego, CA, DARPA Conference on Materials Science  
Los Alamos, NM, LANL-BES Review  
Albuquerque, NM, Sandia, BES Review  
Boston, MA, Winter Mtng, Materials Research Society,  
Session Chair, Editor  
State University of New York, Albany  
U. S. Naval Research Laboratory

A. Barry Kunz  
Funding History (Major Grants)

1971-1976	Contract for "Theory of Correlation in Solids", Aerospace Research Laboratory, Wright-Patterson AFB.
	Initial annual level        ~\$ 10,000
	Final annual level        ~\$ 50,000
	Total award               ~\$150,000
1976-1981	Contract for "Band Theory of Semiconductors", Air Force Office of Scientific Research.
	Initial annual level        ~\$ 50,000
	Final annual level        ~\$ 70,000
	Total award               ~\$300,000
1974-1985	Grant for "Theory of Solids", National Science Foundation via University of Illinois Materials Research Laboratory.
	Initial annual level        ~\$ 70,000
	Final annual level        ~\$180,000
	Total award               ~\$1,210,000
1981-1986	Grant for "Energy Trapping, Release, and Transport in Energetic Solids", Office of Naval Research.
	Initial annual level        ~\$ 50,000
	Final annual level        ~\$ 80,000
	Total award               \$346,000
1984-Present	Grant for "Theory of Defects", Department of Energy
	Current annual level        \$ 96,000
	Total project to date       \$362,000
1985-Present	Grant for "Defects in Non Metals", Office of Naval Research.
	Current annual level        \$278,000
	Total project to date       \$816,000
1986-Present	Contract for "Science Support for Process Rheology", Office of Naval Research, subcontract from Lockheed, Inc.
	Current annual level        \$150,000
	Total project to date       \$300,000

## VITA

### Bryan H. Suits

Bryan H. Suits was born in Ann Arbor, Michigan in the year 1954. While in High School he received several awards for academic achievement in math and physics including a Navy Science Award, an Exxon "Scientist of Tomorrow" award as well as an award from the state of Michigan for his performance on the state wide mathematics contest. He graduated from Ann Arbor Huron High school with honors in 1973.

Dr. Suits continued his education at Carleton College in Northfield, Minnesota. During this time he spent a six month internship at Argonne National Labs studying rare earth hydrides using Mossbauer spectroscopy with Gopal Shenoy and Bobby Dunlap. Upon returning to Carleton he designed and completed a senior project studying gamma ray angular correlations in Pd. He obtained his BA with a major in physics in 1977 magna cum laude and was elected to the honorary fraternities Phi Beta Kappa and Sigma Xi.

From the spring to fall of 1977 he worked at the Environmental Research Institute of Michigan (ERIM) in Ann Arbor. This work centered on the use of computer modeling to establish criteria for the aerial evaluation and identification of vegetation.

In the fall of 1977 he entered graduate school at the University of Illinois at Urbana-Champaign. In the summer of 1978 he began work with Prof. C. P. Slichter studying charge density waves in transition metal dichalcogenides using NMR. This work included growing and characterizing crystalline samples as well as NMR and NQR measurements. In January of 1979 he was granted a Master's of Physics. His Ph.D thesis, titled "Confirmation of McMillan's Concept of Discommensurations in 2H-Tantalum Diselenide" was submitted and accepted in August of 1981. From September 1981 to the fall of 1982 he worked as a research associate with Slichter's group. During this time he designed and performed NQR experiments on the novel conductor niobium triselenide.

In the late fall of 1982 Dr. Suits began work at the University of Pennsylvania as a research associate with the Laboratory for Research on the Structure of Matter with Profs. G. Farrington and David White. This work emphasized the study of ionic motion in the  $\beta$ -alumina family of materials using NMR. While at Pennsylvania, Dr. Suits began his pioneering work on the use of NMR imaging to study solids. In particular, producing images of diffusing ions in the "superionic conducting"  $\beta$ -alumina materials. He also developed and taught an experimental cross-disciplinary course, "Digital Circuitry and Design of Instrumentation", a graduate level special topics course. This course was the first of its kind to be sponsored by the LRSM.

In the fall of 1985, Dr. Suits began his current appointment as an assistant professor with the department of physics at Michigan Technological University. He is developing non-invasive NMR imaging techniques to study damaged solids and to study complex fluid flow in particle filled polymer systems. This work is being supported by two contracts with the Office of Naval Research, the second of which is a joint contract with Lockheed Corporation. Dr. Suits is a member of the American Physical Society and the Society for Magnetic Resonance Imaging.

### Publications

- "Valence Transformation of Eu Atoms Due to Defect Association in Cold Worked EuMg Alloys," R. G. Pirich, C. R. Burr, G. K. Shenoy, B. D. Dunlap, B. Suits and J. D. Phillips, Phys. Rev. Lett. **38**, 1142 (1977).
- "Mossbauer Study of  $\text{Er}^{3+}$  in  $\text{ErH}_3$ ," B. Suits, G. K. Shenoy, B. D. Dunlap, and D. G. Westlake, J. of Magnetism and Magnetic Materials **5**, 344 (1977).
- "Magnetic Properties of Dihydrides and Dideuterides of Er and Ho," J. M. Friedt, B. Suits, G. K. Shenoy, B. D. Dunlap, and D. G. Westlake, J. Appl. Phys. **50**, 2049 (1979).
- "Observation of Newly Discovered 112K Charge Density Wave Transition in  $2\text{H-TaSe}_2$  Using Electrical Resistance", B. H. Suits and M. C. Chen, Phys. Lett. **79A**, 224 (1980).
- "Confirmation of McMillan's Concept of Discommensurations", B. H. Suits, S. Couturie, and C. P. Slichter, Phys. Rev. Lett. **45**, 194 (1980).
- "NMR Test of McMillan's Concept of Discommensurations in  $2\text{H-TaSe}_2$ ", B. H. Suits, S. Couturie, and C. P. Slichter, Phys. Rev. B **23**, 5142 (1981).
- "Thermopower of  $\text{TaS}_3$ ", R. L. Allgeyer, B. H. Suits, and F. C. Brown, Solid State Commun. **43**, 207 (1982).
- "An NQR Study of the 145K CDW Transition in  $\text{NbSe}_3$ ", B. H. Suits and C. P. Slichter, Phys. Rev. B **29**, 41 (1984).
- "NMR Imaging in Solids", B. H. Suits and David White, Solid State Commun. **50**, 291 (1984).
- "Chemical Shifts of Lead Halides", B. H. Suits and David White, In preparation.
- "Nuclear Magnetic Resonance Imaging of Temperature Profiles", B.H. Suits and David White, J. Appl. Phys. **60**, 3772 (1986).

"A Nuclear Magnetic Resonance Study of Al-Mn Quasicrystals and Related Materials", K. R. Carduner, B. H. Suits, J. A. DiVerdi, M. D. Murphy and David White, J. Mater. Res. 2, 431 (1987).

"Imaging Electromagnetic Fields Using the Magnetic Resonance of a Paramagnetic Gas", S. A. Marshall, B. H. Suits, M. T. Umlor, and U. N. Zhang, to be published in J. Magn. Reson.

"An NMR Study of Li in AlLiCu Icosahedral Alloys", C. Lee, David White, B. H. Suits, P. A. Bancel, and P. A. Heiney, submitted to the Physical Review.

#### Reports

J. Robert Maxwell and Bryan Suits, ERIM reports 127600-7-f (190 pgs) and 127600-3-f (134 pgs) for the U.S. Dept. of Justice, Contract DEA-77-6.

#### Significant Presentations

"NMR Confirmation of McMillan's Concept of Discommensurations", Invited talk for the Division of Condensed Matter Symposium on CDW's and SDW's in Incommensurate Systems, March Meeting of the American Physical Society, Phoenix (1981).

"NMR Imaging in Solids", Invited talk for the FACSS fall meeting in Philadelphia (1985).

Biographical Sketch.

S. A. Marshall, Jr.

<b>Present Position:</b>	Professor, Department of Physics Michigan Technological University.
<b>Telephone:</b>	906/487-2900 (work), 906/482-5242 (home)
<b>Mailing Address:</b>	Department of Physics, Fisher Hall Michigan Technological University Houghton, Michigan 49931.
<b>Education:</b>	Ph.D. (physics) The Catholic University of America, Washington, D.C., M.S. (physics) The University of Michigan, Ann Arbor, Michigan, B.S. (physics) The Illinois Institute of Technology, Chicago, Illinois.
<b>Professional Experience:</b>	1981- , Professor Department of Physics, Michigan Technological University, Houghton, Michigan. 1963-1981, Research Scientist, Solid State Sciences Division, Argonne National Laboratory, Argonne, Illinois. 1956-1963, Senior Research Scientist, IIT Research Institute, Chicago, Illinois. 1952-1956, Physicist, U.S. Naval Ordnance Laboratory, White-Oak, Silver Spring, MD. 1951-1952, Physicist, National Bureau of Standards, Washington, D.C.
<b>Research Interests:</b>	Physics of Solids: Magnetic Defects in Nearly Perfect Crystals; Paramagnetic Resonance Absorption Spectroscopy of Transition Metal Ions and Free-Radical Molecule Ions in Solids and Liquids; Nuclear Magnetic Resonance Spectroscopy in Hydrides and Superionic Conductors; Crystal Field Theory; Hyperfine Interactions; Color Centers in Alkali Halide Crystals.
<b>Organization Membership:</b>	The American Physical Society (1952), The Society of Sigma Xi (1956), A.A.A.S. (1956), The Physics Club of Chicago (1958).
<b>Additional Professional Activities</b>	1956-57, Visiting Scientist at the U.S. Naval Ordnance Laboratory where some design work was done on a high temperature

microwave spectrometer. 1957-62, On various occasions during this period taught graduate and undergraduate courses at the Illinois Institute of Tech. 1960-63, Directed one M.S. and two Ph.D. thesis programs at the Ill. Inst. of Tech. 1964, Attended a summer institute at the University of Colorado (Boulder) on the Theory of Groups and on the Lorentz Group. 1965-present, Taught a course on Electron Spin Resonance Absorption Spectroscopy at a NATO summer school in Freiburg, W. Germany; directed the research of approximately 20 honors students at the average of two students per year; referee of papers to scientific journals such as The Physical Review, The Journal of Magnetic Resonance, The Journal of Physics and Chemistry of Solids, The Journal of Physical Chemistry, and others on occasion.

For about seven years, held position of adjunct professor of physics at the Northern Illinois University where an M.S. thesis was directed during the last two years of the appointment.

During the 1970-71 participated in a program of research with Dr. S. V. Nistor of the Institute of Atomic Physics, Bucharest, Romania. The program was sponsored in part by the National Science Foundation (U.S.A.), the Ministry of Science and Culture (Romania) and the U.S. Atomic Energy Commission.

**Academic  
Research  
Supervision:**

1960, Irving Segal, M.S. in physics at the Illinois Institute of Technology.  
1962, Dickron Mergerian, Ph.D. in physics at the Illinois Institute of Technology.  
1965, Raymond R. Serway, Ph.D. in physics at the Illinois Institute of Technology.  
1970, Joachim Doepler, M.S. in physics at the Illinois Institute of Technology.

**Publications:**

36. Temperature Dependence of the Hyperfine Structure Splitting of Divalent Manganese in Single Crystal Calcite.  
C. Y. Huang, R. S. Kent and S. A. Marshall, Phys. Rev. B7, 552 (1973).



37. Temperature Dependence of the Hyperfine Structure Splittings of Some Trioxide Molecule Ions in Single Crystal Calcite.  
R. A. Serway, S. L. Chan and S. A. Marshall, Phys. Stat. Sol. (b)57, 269 (1973).
38. Determination of the Debye Temperature of Thorium Oxide from ESR Measurements.  
S. V. Nistor and S. A. Marshall, XVII Congress Ampere, V. Hovi, Ed. (North-Holland Publ. Col., 1973).
39. Evidence for Strain Broadening in the ESR Absorption Spectrum of Tetragonally Distorted Trivalent Chromium Ions in Magnesium Oxide.  
R. A. Serway, R. B. Robinson and S. A. Marshall, Phys. Stat. Sol. (b)56, 319 (1973).
40. Temperature Dependence of the Hyperfine Interaction of Trivalent Gadolinium in Single Crystal Thorium Oxide.  
S. A. Marshall, S. V. Nistor, C. Y. Huang, and T. Marshall, Phys. Stat. Sol. (b)59, 55 (1973).
41. Temperature Dependence of the Hyperfine Structure Coupling Parameters of the Monovalent Carbon Dioxide and Divalent Arsenic Dioxide Molecule Ions in Irradiated Single Crystal Calcite.  
S. S. Chan, S. A. Marshall and R. A. Serway, Phys. Stat. Sol. (b)59, 687 (1973).
42. Superhyperfine structure in the ESR Spectra of the Monovalent Carbon Dioxide and the Trivalent Carbonate Molecule Ions in Irradiated Single Crystal Calcite.  
S. A. Marshall, J. A. McMillan and R. A. Serway, J. Mag. Res. 14, 20 (1974).
43. Electron Spin Resonance Absorption Spectrum of the Divalent Bicarbonate Molecule Ion in Irradiated Single Crystal.  
Jean Cass, R. S. Kent, S. A. Marshall and S. A. Zager, J. Mag. Res. 14, 170 (1974).
44. Tentative Identification by ESR of a  $\text{CSO}_2^{\cdot -}$  Impurity Ion Irradiated Single Crystal Calcite.  
R. L. Marshall, W. D. Ohlsen, S. A. Marshall and R. A. Serway, J. Mag. Res. 15, 89 (1974).
45. Comments on the Magnetic Resonance Absorption Spectrum of the (F-F) Molecule Ion in Single Crystal LiF, NaF, and KF.  
S. A. Marshall, Phys. Stat. Sol. (b)82, 311 (1977).
46. Electron Spin Resonance Absorption Spectroscopy Investigation of Magnetic Impurities in Single Crystal Yttrium Aluminum Garnet.  
S. A. Marshall, T. Marshall and R. A. Serway, Proc. Int. Conf. on Defects in Insulating Crystals, Gatlinburg, Tenn. (1977).
47. Electron Spin Resonance Absorption Spectrum of Trivalent Gadolinium in Single Crystal Yttrium Aluminum Garnet.  
S. A. Marshall, T. Marshall and R. A. Serway, Phys. Stat. Sol. (b)48, 165 (1978).
48. Line Broadening in the ESR Absorption Spectrum of the Trivalent Ions of Iron, Chromium and Gadolinium.  
R. A. Serway, F. H. Huang and S. A. Marshall, Phys. Stat. Sol. (b)89, 267 (1978).

49. Electron Spin Resonance Absorption Spectrum of Divalent Manganese in Single Crystal Calcite.  
S. A. Marshall, T. Marshall, S. A. Zager, D. N. Zimmerman, Phys. Stat. Sol. (b) 91, 275 (1979).
50. Photo and Thermal Reactions in Single Crystal Corundum Doped with Vanadium Oxide and Cobalt Oxide.  
C. J. Delbecq, S. A. Marshall and P. H. Yuster, Phys. Stat. Sol. (b) 99, 377 (1980).
51. Structural Phase Change in the Fast Ion Conductor Sodium Scandium Phosphate.  
C. J. Delbecq, S. A. Marshall and S. Susman, Solid State Ionics 1, 145 (1980).
52. Dielectric Properties of the Fast Ion Conductor Sodium Scandium Phosphate.  
C. J. Delbecq, S. A. Marshall and S. Susman, Phys. Stat. Sol. (b) 106, 731 (1981).
53. ESR Absorption Spectrum of Trivalent Gadolinium in Single Crystal Yttrium Desquioxide.  
S. A. Marshall, T. Marshall and P. H. Yuster, Phys. Rev. B25, 1505 (1982).
54. The ESR Absorption Spectrum of the (110) Oriented  $\{F-Cl\}^-$  Molecule Ion in Single Crystal KF Doped with KCl and AgCl.  
C. J. Delbecq, Elson Hutchinson, S. A. Marshall and P. H. Yuster, J. Chem. Phys. 79, 1408 (1983).
55. Comments on the ESR Absorption Spectrum of Tetragonally Distorted Trivalent Chromium in Magnesium Oxide.  
Mark Parent and S. A. Marshall.  
Submitted for publication, American Journal of Physics.
56. A Development of the Racah Polynomials Operators of Orders One to Twelve.  
S. A. Marshall, T. Marshall and H. A. Buckmaster.  
Accepted for publication by J. Mag. Res. (1988).
57. Imaging Electromagnetic Fields Using the Magnetic Resonance Absorption Spectrum of a Paramagnetic Gas.  
S. A. Marshall, B. H. Suits, M. T. Umlor, and Y. N. Zhang.  
Accepted for publication by J. Mag. Res.

#### Manuscripts in Preparation

1. The ESR Absorption Spectrum of the Orthorhombically Symmetric Tetravalent Chromium Ion in Single Crystal Corundum.  
S. Marshall, and T. Marshall.
2. Superhyperfine Structure in the ESR Spectrum of Divalent Manganese in Magnetically Dilute Zinc Selenide.  
S. A. Marshall, D. R. Yoder-Short, Y. N. Zhang, and J. K. Furdyna.

Vita

CHRISTOPHER WOODWARD

Academic Rank:

Assistant Professor

Research Interests:

Solid State Physics, Molecular Physics.

Education:

Ph.D., University of Illinois at Champaign Urbana September 1985,  
A. B. Kunz Advisor.  
M.S., University of Illinois at Champaign Urbana January 1983.  
B.S., University of Massachusetts at Amherst September 1979.

Experience:

10/85- Assistant Professor, Department of Physics, Michigan  
Technological University Houghton, Michigan.

9/84- Physics Graduate Student in ab-sentia from the University  
9/85 of Illinois at Champaign Urbana. Instructor, Department of  
Physics, Michigan Technological University, Houghton  
Michigan.

5/84- Consultant to the Theoretical Physics Division at the  
8/84 A.E.R.E. Harwell England.

5/82- Research Assistant at the University of Illinois  
5/84 Materials Research Laboratory.

8/81- Teaching Assistant, Department of Physics, the University  
5/82 of Illinois at Champaign Urbana.

6/79- Research Assistant at the Raytheon Semiconductor  
6/80 Laboratory in Waltham, Massachusetts.

8/76- Research Technician with the Medium Energy Nuclear  
6/79 Physics group at the University of Massachusetts at  
Amherst.

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Michigan Technological University  
Houghton, MI 49931.

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Born: January 19, 1957 in Quincy, Massachusetts USA.

Honors and Societies:

American Physical Society  
Member of APS Summer Intern Program 1979.  
Cum Laude (B.S.)  
National Honor Society President 1975.

Research Activities:

Research is devoted to developing and implementing models to study defects and local excitations in solids. The current thrust of my work is to use norm-conserving pseudopotentials in a variety of methodologies and to exploit the pseudopotential method.

X-Ray Edge in Alkali Alloys.

This is an ab-initio study of local excitations in alkali alloys using the Hartree Fock method with the inclusion of electron correlation effects treated using many body perturbation theory. The cluster model and pseudopotentials are used to simulate the bulk. The research parallels recent experimental work by C. P. Flynn et. al. (University of Illinois) and gives theoretical justification for their results.

Ionic Crystal with Electronic Cluster: Automated Program.

This self-consistent lattice relaxation and electronic structure program is the result of an international collaboration between the University of Illinois, the A.E.R.E. Harwell England and the University of Manitoba. ICECAP is a program for performing calculations of the electronic structure of defects in ionic crystals using a Hartree Fock pseudopotential cluster embedded in a consistently relaxed shell model lattice. This permits a physically accurate description of defect centers for cases where there is a strong localized perturbation of the electronic structure of the lattice.

## Hartree Fock Monte-Carlo.

This work investigates the use of the Hartree-Fock method in a Monte-Carlo environment. Using the pseudopotential method with optimized algorithms it is possible to study the diffusion of impurities, phase transitions and the geometry of molecular systems. This is an international collaboration between myself, G. Jacucci (Trento, Italy) and G. Delorenzi (Lawrence Livermore National Laboratory).

### Publications:

1. "Hartree-Fock Cluster Computations of Defect and Perfect Ionic Crystal Properties", J. H. Harding, A. H. Harker, P. B. Keegstra, R. Pandey, J. M. Vail, and C. Woodward, Proceedings 1984 Norwich Conference. To be published Physica 1985.
2. "Search for 2hw M1 Transitions in 208 Pb", C. Woodward and G. Peterson, Phys. Rev. C20, 2437 (1979).

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